

SPECIFICATION

TITLE OF THE INVENTION

METHOD FOR MANUFACTURING A SEMICONDUCTOR DEVICE

5 BACKGROUND OF THE INVENTION

The present invention relates to a manufacturing method of a semiconductor device, particularly to a manufacturing method of a semiconductor device, which comprises, during manufacture of the semiconductor device, plasma etching metal films including aluminum (Al).

In plasma etching of a metal material, it is the common practice to use a plasma of a mixture gas of Cl_2 and BCl_3 which are leading etching gases.

For microfabrication process, in addition to such gases, a CCl_4 gas, a CHCl_3 gas, an N_2 gas, a CHF gas or a gas obtained by diluting a flammable and explosive CH gas to not greater than an explosion limit is usually added as a shape controlling gas, in other words, as an undercut preventive gas. In Japanese Patent Application Laid-Open No. 251984/1997, proposed is a method of adding a CHBr gas as a shape controlling gas.

Among the shape controlling gases to be added upon plasma etching of a metal material, production of a CCl_4 gas is limited because it is an ozone depleting substance. Production of a CHCl_3 gas tends to be decreased owing to its carcinogenicity.

In a gas such as CHF gas containing an F element, AlF

generated upon etching reaction forms particles having a large particle size. These particles cause a yield reduction so that this gas is not suited for mass production. Also in the case of an N_2 gas, AlN generated upon etching reaction forms particles so that it is not suited for mass production.

A Br-containing gas such as CHBr gas forms, on the side walls of a minute pattern during etching, a markedly strong side-wall protection film for shape control. This side-wall protection film cannot be removed by treatment with a chemical liquid. Adiluted CH gas, on the other hand, contains only several percent of a C element having a shape controlling action so that it is accompanied with such a drawback as small shape controlling effects.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an etching method which uses a gas suppliable stably also in future, is reduced in the problem of particle contamination, is free from the difficulty in removal of side-wall protection films, and has high shape controlling capacity, and a manufacturing method of a highly reliable semiconductor device by using this etching method.

In the present invention, a CH_2Cl_2 gas is used as an additive gas for shape control. Described specifically, a metal material is etched by a plasma of a mixture of a Cl_2 gas, a BCl_3 gas and

a CH_2Cl_2 gas.

The specific and typical constitution of the present invention will next be described. In one aspect of the present invention, there is thus provided a manufacturing method of a semiconductor device which comprises depositing metal film including an aluminum over a semiconductor substrate and etching the metal film by using a plasma of a mixture of a Cl_2 gas, a BCl_3 gas and a CH_2Cl_2 gas.

In another aspect of the present invention, there is also provided a manufacturing method of a semiconductor device, which comprises, upon formation of multilayer interconnects of an aluminum-containing metal over a semiconductor substrate, etching of the metal interconnects by using a plasma of a mixture of a Cl_2 gas, a BCl_3 gas and a CH_2Cl_2 gas.

In a further aspect of the present invention, there is also provided a manufacturing method of a semiconductor device, which comprises forming metal films over a semiconductor substrate by stacking a TiN film, an Al film and a TiN film one after another; and etching the metal films by using a plasma of a mixture of a Cl_2 gas, a BCl_3 gas and a CH_2Cl_2 gas, wherein the amount of CH_2Cl_2 gas is adjusted to 0 to 4% upon etching of the TiN film, while it is adjusted to 5 to 30% during etching of the Al film.

In a still further aspect of the present invention, there is also provided a manufacturing method of a semiconductor device,

which comprises depositing metal film including an aluminum over a semiconductor substrate, forming a resist mask over the metal film, etching the metal film by using a plasma of a mixture of a Cl_2 gas, a BCl_3 gas and a CH_2Cl_2 gas and removing a resist mask by using a plasma of a mixture containing an F element and an O element.

In a still further aspect of the present invention, there is also provided a manufacturing method of a semiconductor device, which comprises depositing metal film including an aluminum over a semiconductor substrate, forming patterns at a wiring pitch less than 500 nm over the metal film, and etching the metal film with a plasma of a mixture gas containing a Cl_2 gas, a BCl_3 gas and a CH_2Cl_2 gas.

In a still further aspect of the present invention, there is also provided a manufacturing method of a semiconductor device, which comprises depositing metal film including an aluminum over a semiconductor substrate, forming a first mask pattern group (or a first pattern group) at a first pitch and then, a second mask pattern group (or a second pattern group) at a second pitch over the metal film, and etching the metal film by using a plasma of a mixture of a Cl_2 gas, a BCl_3 gas and a CH_2Cl_2 gas.

In a still further aspect of the present invention, there is also provided a manufacturing method of a semiconductor device, which comprises forming metal films over a semiconductor substrate by stacking a TiN film, an Al film and a TiN film one

after another, and etching the metal films by using a plasma of a mixture of a Cl_2 gas, a BCl_3 gas and, as an additive gas, a CH_2Cl_2 gas diluted with a diluting gas, wherein the mole concentration of the CH_2Cl_2 gas diluted with the diluting gas is 10% to 100%.

In a still further aspect of the present invention, there is also provided the above-described constitutions, wherein the pressure of the mixture gas is not greater than 1.5 Pa but 0.6 Pa or greater; the CH_2Cl_2 gas has a purity of at least 99.99%; and the plasma is generated using an electromagnetic wave having a frequency range of 300 MHz to 1 GHz (UHF range).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the characteristics of various additive gases;

FIG. 2 illustrates the relationship between a ratio of failure by particle contamination and the number of wafers treated;

FIG. 3 illustrates the relationship between the CD shift relative to a resist mask and the kind of additive gases;

FIG. 4 is a cross-sectional view, after washing treatment, of a sample etched with a CH_2Br_2 -containing gas;

FIG. 5 is a cross-sectional view, after washing treatment, of a sample etched with the CH_2Cl_2 -containing gas of the present invention;

FIG. 6 is a flow chart for explaining one example of a multilayer interconnection step of a semiconductor device to which the etching method of the present invention is applied;

FIG. 7A illustrates the cross-sectional structure of a sample used for metal etching, whereas FIG. 7B illustrates one example of the etching results of the sample (Fig. 7A);

FIG. 8 illustrates the relationship between a wiring pitch and undercut condition; and

FIG. 9 illustrates the relationship between the CD shift of patterns formed at a wiring pitch of 100 nm and a dilution ratio of CH_2Cl_2 when the sample of FIG. 7A is etched with a mixture gas containing a CH_2Cl_2 gas diluted with Ar.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Example 1)

Results of comparison between a CH_2Cl_2 gas and another gas in their characteristics such as ozone layer destructivity, carcinogenicity and inflammability are shown in FIG. 1.

A CH_2Cl_2 gas used in the present invention is, different from a CCl_4 gas or a CHF gas, free from the problem of ozone layer destruction and is, different from a CHCl_3 gas, has no carcinogenicity. There is accordingly a high possibility of it being supplied stably in future. Different from a CH gas or another CHCl gas, it is flame retardant so that it can be added without dilution. Different from a CHF gas or an N_2 gas,

it does not contain elements such as N and F, which tends to make it free from the problem of particle contamination.

Different from a CHBr gas, it does not contain Br so that it is presumed not to be troubled much with the problem in

5 removability of a side-wall protection film.

Generation of particles was studied using a CH₄ gas diluted to 8% with Ar (which will hereinafter be described as "PR gas"), a CH₂Cl₂ gas, a CH₂Br₂ gas, a CHF₃ gas and an N₂ gas, respectively. In FIG. 2, shown is the relationship - when a wafer having a metal material thereon is etched with a plasma of each of various gases and a Cl₂-BCl₃ mixture gas - between a ratio of failure by particle contamination and the number of wafers treated. It is however to be noted that during etching, plasma cleaning in a chamber is conducted by using O₂ gas plasma discharge or Cl₂ gas plasma discharge.

When the number of the wafers etched with a plasma of a mixture gas containing an N₂ gas or a CHF₃ gas is 500, the failure ratio reaches 90% or greater. So this gas is not suited for mass production. When the number of the wafers treated with a plasma of a mixture gas containing a CH₂Cl₂ gas, a CH₂Br₂ gas or a PR gas is 5000, on the other hand, the failure ratio is suppressed to less than 10%, suggesting that this gas is suited for mass production.

In the next place, shape control was studied. A PR gas, a CH₂Cl₂ gas, or a CH₂Br₂ gas suited for mass production was selected

as an additive gas, and a sample was etched using a plasma of a mixture gas containing the additive gas, a Cl_2 gas and a BCl_3 gas. The sample employed here was a wafer which had a diameter of 8 inches, had thereover TiN, Al and TiN films successively stacked one after another, and had a resist film formed over these stacked films. In FIG. 3, the relationship among a CD shift relative to the resist mask, an etching rate and kinds of gases added. In this diagram, an etching rate (nm/min) is indicated by a circle.

When the partial pressure of a Cl_2 gas is low, a decrease in an etching rate occurs. It is necessary to maintain the partial pressure of a Cl_2 gas at about 0.5 Pa or greater in order to maintain an etching rate at 600 nm/min or greater which is sufficient for practical use. Since high treating pressures cause an increase in the CD shift, it is necessary to suppress the treating pressure to 1.5 Pa or less in order to attain a practically usable CD shift of 100 nm or less. In addition, it is necessary to add a shape controlling gas in an amount of about 20% of the Cl_2 gas in order to suppress side etching.

In a PR gas, the shape controlling CH_4 gas has been diluted to 8%, so that the PR gas should be added in an amount of about 2.5 times as much as that of the Cl_2 gas in order to control the shape. This increases the treating pressure to about 3.5 times as much as the partial pressure of the Cl_2 gas, making it difficult to attain both a sufficient etching rate and a

sufficient CD shift. Addition of a PR gas, which has been adjusted to maintain an etching rate at a practically usable level of 600 nm/min as shown in FIG. 3, increased a CD shift as large as several hundred nm or greater.

5 A CH_2Cl_2 gas or CH_2Br_2 gas is, on the other hand, usable without diluting a shape controlling gas. Even by the addition of a 20% shape controlling gas, the treating pressure can be suppressed to about 1.2 times as much as that of the Cl_2 partial pressure. This makes it possible to attain both a sufficient
10 etching rate and sufficient CD shift within a wide range from 0.6 Pa to 1.5 Pa. As a result, a CH_2Cl_2 gas and a CH_2Br_2 gas can suppress the CD shift to about 10 nm while maintaining an etching rate at a practically usable level of 800 nm/min.

As described above, it has been found that a CH_2Cl_2 gas
15 and a CH_2Br_2 gas are much superior in shape controllability to a PR gas.

After removal of the resist mask by a plasma of a CF_4 and O_2 mixture gas from the sample etched with each of a CH_2Cl_2 gas and CH_2Br_2 gas, the resulting wafer was washed with a mixed solution
20 of acetic acid and aqueous ammonia. The cross-sectional views of the sample after washing are shown in FIGS. 4 and 5.

As is apparent from FIG. 4 wherein the shape after etching with a CH_2Br_2 gas is illustrated, a side-wall protection film
4 remains on the side walls of the barrier TiN layer 1, Al layer
25 2 and cap TiN layer 3 and over the cap TiN layer 3, suggesting

that the side-wall protection film cannot be removed completely by the washing after etching. Indicated at numeral 5 in these diagrams is a semiconductor substrate.

As is apparent from FIG. 5 wherein the shape after etching with a CH_2Cl_2 gas is illustrated, the side-wall protection film is removed completely from the side walls of the barrier TiN layer 1, Al layer 2 and cap TiN layer 3 and from the upper surface of the cap TiN layer 3, suggesting that this gas is superior in removability of the side-wall protection film. For the removal of the resist mask, a plasma of a CF_4 and O_2 mixture gas was employed. Similar results are available insofar as the plasma is a mixture gas containing an F element and O element.

It has been understood from the above-described results that use of a CH_2Cl_2 gas as an additive gas for shape control is desired from four viewpoints, that is, stable gas supply, suitability for mass production, shape controllability and removability of side-wall protection films.

(Example 2)

In etching of a stacked structure of a TiN film, an Al film and a TiN film formed over a semiconductor substrate, the amount of a CH_2Cl_2 gas is suppressed to 0 to 4% upon etching of the TiN film and it is increased to 5 to 30% only during etching of the Al film which needs shape control. This makes it possible to decrease the CD shift to half of that in the case of etching without changing the amount of the gas.

(Example 3)

FIG. 6 illustrates an application example of the etching method of the present invention to a multilayer interconnection step of a semiconductor device. In this interconnection step, a via hole is made by successively carrying out (1) deposition of a silicon oxide film (TEOS) by chemical vapor deposition (CVD), (2) formation of a resist mask by photolithography and (3) etching of TEOS by using a plasma of a CF gas along the resist mask. In the resulting via hole, (4) TiN is embedded by sputtering, followed by (5) embedding of tungsten (W) by CVD.

Excessive W and TiN deposited over the TEOS surface by the above-described embedding step is (6) removed by chemical mechanical polishing (CMP) and then, (7) washed with a chemical solution. After successive deposition, over the TEOS surface after CMP, of (8) TiN by sputtering, (9) Al-Cu mixed crystals by sputtering, (10) TiN by sputtering, (11) TEOS by CVD, and (12) SiON by CVD, (13) the resist mask is patterned by lithography. Along this resist mask, TEOS is (14) etched by a CF gas to form a TEOS mask.

Along the TEOS mask thus formed, the TiN, Al-Cu and TiN films thus stacked are etched using a plasma of a mixture gas of Cl_2 , BCl_3 and CH_2Cl_2 according to the present invention. After etching, the remaining resist mask is (16) removed by a plasma of a mixture gas of O_2 and CF_4 , followed by (17) washing with a chemical solution.

After (18) deposition of an insulating material over the washed sample by CVD, the resulting sample is (19) planarized by CMP and then (20) washed with a chemical solution. The resulting sample is subjected to the above-described steps starting from (1) in repetition, whereby a multilayer interconnection is formed.

The yield of the semiconductor device produced in accordance with the method of the present invention which uses a CH_2Cl_2 gas for the etching step (15) was 90%. The yield of the semiconductor device produced using a PR gas in the step of (15) was, on the other hand, only 50% owing to disconnection failure or short-circuit failure. The yield lowered to 40% by the use of a CH_2Br_2 gas, because of high contact resistance. The yield drastically decreased to 10% by the use of a CHF_3 gas owing to particle contamination.

As described above, in the multi-layer interconnection step including an aluminum film, use of a plasma of a mixture gas of Cl_2 , BCl_3 and CH_2Cl_2 for etching of a metal interconnection makes it possible to fabricate a semiconductor device having a high reliability.

(Example 4)

As illustrated in FIG. 7A, a sample having various line and space patterns formed using a resist mask 6 over a stacked structure of a barrier TiN film 1, an Al film 2 and a cap TiN film 3 over a semiconductor substrate 5 was etched using a plasma

of a mixture gas containing Cl_2 , BCl_3 and an undercut preventive gas.

One example of the etched shape is shown in FIG. 7B. Patterns of a wide pitch can be etched vertically, whereas those of a fine pitch have undercut appeared on the Al film 2.

In FIG. 8 illustrated are the results of the undercut conditions in the patterns formed at wiring pitches of 1000, 500, 300, 260 and 200 when a PR gas or CH_2Cl_2 gas was used as an additive gas. At wiring pitches of 500 nm or greater, no undercut was observed irrespective of the kind of the additive gas. At wiring pitches less than 500 nm, undercut appeared when a PR gas was added, while it was suppressed when a CH_2Cl_2 gas was added. This suggests that addition of a CH_2Cl_2 gas has marked effects on the patterns formed at a wiring pitch less than 500 nm.

(Example 5)

A difference in the CD shift between the pattern formed at a wiring pitch of 1000 nm and that formed at a wiring pitch of 200 nm was measured using the sample obtained in Example 4. As a result, the difference in CD shift was as large as 200 nm in the case of PR gas addition, whereas it was as small as 20 nm in the case of CH_2Cl_2 gas addition. This suggests that addition of a CH_2Cl_2 gas is effective for etching of a sample on which patterns different in wiring pitch exist on the same wafer.

(Example 6)

Upon preparation of the sample of Example 4, a CH_2Cl_2 gas having a purity of 99.9% was added, resulting in problems of foreign matters and metal contamination. It has been understood that such problems do not occur when a CH_2Cl_2 gas having a purity of 99.99% or greater is used.

(Example 7)

The sample as illustrated in FIG. 7A was etched using a plasma of a mixture gas containing a Cl_2 gas, a BCl_3 gas and an undercut preventive gas. As this undercut preventive gas, a CH_2Cl_2 gas diluted with Ar was employed. In FIG. 9, the relationship between the CD shift of the patterns formed at a wiring pitch of 1000 nm and a dilution ratio of CH_2Cl_2 is illustrated.

The CD shift increases with a dilution ratio. At a mole concentration of CH_2Cl_2 not less than 10%, however, CD shift is smaller compared with the case where a PR gas is added. It has been found that when a CH_2Cl_2 is diluted with Ar to give a mole concentration of 10% to 100%, the shape controllability is higher, compared with the use of a conventional gas. For dilution, Ar was employed here, but there is no limitation imposed on the dilution gas insofar as it is inert.

(Example 8)

The sample obtained in FIG. 7A was etched with a mixture gas of Cl_2 , BCl_3 and CH_2Cl_2 by using each of an etching system which generates a plasma by using an UHF-range electromagnetic

wave (300 MHz to 1 GHz) (which system will hereinafter be called "UHF plasma etching system), an etching system which generates a plasma by using an electromagnetic microwave (2.45 GHz) (which system will hereinafter be called "microwave etching system", and an etching system which generates a plasma by using an RF-range electromagnetic wave (13.56 MHz or less) (which system will hereinafter be called "ICP plasma etching system).

As a result, the UHF plasma etching system did not cause undercut easily compared with the microwave plasma etching system or ICP etching system. In the microwave plasma etching system or ICP etching system, a plasma density is high and this facilitates dissociation of CH_2Cl_2 into the corresponding atoms so that effects of gas addition are reduced by half. It is presumed that in the UHF plasma etching system, on the other hand, a plasma density is low and this disturbs dissociation of a CH_2Cl_2 gas, effects of the additive gas tend to appear readily. (Example 9)

In Example 3, the resist was removed in the step 16 after etching of the stacked films of TiN, Al-Cu and TiN in the step 15. In this Example, after etching of SiON and TEOS in the step 14, the resist removal of the step 16 is conducted, followed by etching of the stacked films of TiN, Al-Cu, and TiN of the step 15. Even after such a permutation, similar results are available.

In Example 3, TEOS was deposited over TiN in the step 11.

Similar results are available even if deposition of SiON over TiN in the step 12 is conducted without the step 11.

As described above, a highly reliable semiconductor device can be manufactured by using the manufacturing method of the present invention adopting an etching method which uses a gas
5 suppliable stably also in future, is reduced in the problem of particle contamination, is free from the problem in the removal of a side-wall protection film and exhibits high shape controlling capacity.

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